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CarbonNanoTubes (CNT) in Bipolar Plates for PEM Fuel Cell Applications

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Abstract

Using standard mass production techniques for the fabrication of fuel cell components, such as bipolar plates, is a main issue for the commercialisation of PEM fuel cell systems. Bipolar plates contribute significantly to the cost structure of PEM stacks. In an upcoming fuel cell market a large number of bipolar plates with specific high-quality standards will be needed. At the Centre for Fuel Cell Technology (ZBT) together with the University of Duisburg-Essen fuel cell stacks based on injection moulded bipolar plates have been developed and demonstrated successfully [1]. This paper focuses on the interactions between carbon filling materials (graphite, carbon black and carbon nanotubes (CNT)) in compound based bipolar plates and especially the potential of CNTs, which were used in bipolar plates for the first time. The entire value added chain based on the feedstock, the compounding and injection moulding process, the component bipolar plate, up to the operation of a PEM single fuel cell stack with CNT-based bipolar plates is disclosed.

1 Introduction

Besides the membrane-electrode-assemblies (MEA) and the gas-diffusion-layers, the bipolar plates constitute the most important element of a PEM fuel cell stack with manifold functions. Bipolar plates work as both electrical and thermal conductive plate between the active cells. They separate the reactant gases and distribute them on each side over the whole active area of the MEA. Finally, they serve as structural element distributing mechanical forces. An important require of property of bipolar plates is their chemical resistance to the operation conditions inside a fuel cell stack. In essence, the bipolar plate material used for low temperature PEM-FCs has to endure a steady electrical potential, a wet environment of pure water, a low pH-value and temperatures of about 80 °C [2].

One way to fulfil all the requirements for bipolar plates combined with the possibility of mass production leads to carbon filled polymer materials for bipolar plates. The development of such compound materials is focused in various of investigations [3,4]. The polymeric matrix allows usage of conventional processing methods such as extrusion for the production of compounds and the further processing to bipolar plates via injection moulding. One main requirement of bipolar plates is a good electrical and thermal conductivity. In order to achieve adequate conductivities for the bipolar plates the (therefore used) compound material normally consist of a polymer which functions as a binding matrix, and a high load (ca. 80 wt%) of carbon-based electrically and thermally conductive filling materials such as graphite and carbon blacks [5]. In the recent years carbon nanotubes seem to be another promising filler material due to their favourable electrical and mechanical properties [6]. Carbon nanotubes have the potential to improve the properties of such highly filled compounds when used in combination with other filler materials. CNTs generally form large agglomerates and the biggest challenge is to disentangle and to disperse the CNT-agglomerates during the process of melt-compounding. To incorporate the CNT homogenously distributed into a polymeric matrix is necessary to achieve high conductivities of such materials even at low CNT content. This plays a key role to transfer the unique properties of CNTs into compound materials. The production of such high filled compound materials can be done by using a kneader or an extruder. In a following step the compound materials are used to produce bipolar plates by injection moulding or compression moulding.

The first objective of this work has been the determination of the influence of different carbon filling materials, especially CNTs, in a polymeric matrix regarding the production process. The second aim focuses on the final properties such as electrical conductivities of injection moulded samples. Finally the effect of this carbon fillers on the performance of a single PEM fuel cell stack has been investigated. The intention of this study is the development of new CNT-based compound materials with improved properties in comparison to carbon black compounds for bipolar plates.

2 Experimental

2.1 Compounding of high filled polymeric materials

As mentioned before a high content of carbon filling materials has to be incorporated into a polymeric matrix to achieve good conductivities. Therefore five highly filled polymer compounds have been processed in a small compounder (kneader, Thermo Scientific Rheomix 3000p) under similar process conditions for benchmarking. Within the scope of this investigation, all compounds have been produced with a similar filling load of 87 wt% to ensure processability and comparability. To explore the interacting dependencies between the filling materials graphite and carbon black or CNTs the following binary and hybrid compounds have been investigated:

- binary compound: graphite (87 wt%) in polypropylene
- hybrid compounds: graphite (84,5 wt%) with a secondary filling material; carbon black (2,5 wt%) or CNTs (2,5 wt%) in polypropylene
- hybrid compounds: graphite (82 wt%) with a secondary filling material; carbon black (5 wt%) or CNTs (5 wt%) in polypropylene

2.2 Injection moulding of samples und bipolar plates

In general ZBT has chosen the injection moulding technique as a standard production method to manufacture bipolar plates in a one-step process with process cycle times below 18 seconds (Kraus Maffei, Germany, F_{max}=3000 KN, p_{max}=350 MPa). The injection moulding of such high filled compound materials is not trivial because of the high melt viscosities of the compounds. Nevertheless it is possible to produce bipolar plates for usage in PEM fuel cells by injection moulding. To achieve a reproducible and fast characterisation of different compound materials, small unstructured plates (diameter = 30 mm, thickness = 2 mm) were injection moulded on a small piston injection moulding machine (Thermo Scientific HAAKE MiniJetII, p_{max} = 120 Mpa).

2.3 Measurement of electrical conductivity

For measurement of through plane electrical conductivity a four pole measurement apparatus is used. The injection moulded samples were placed between two gas diffusion layers (W.L. Gore & Associates GmbH) which are fixed on gold plated stainless steel stamps integrated in a hydraulic press. The measurements were performed under pressure to simulate the operating conditions of a PEM fuel cell. A pressure of 2 Mpa and a current of 500, 1.000, 1.500 and 2.000 mA (Wenking HP 96-20) was applied and the resulting voltage recorded.

2.4 Analysis of internal material structures

Images from scanning electron microscope (field emission-SEM) (Leo 1530 Gemini) give an idea about the internal structure and dispersion of nano particles between graphite flakes at injection moulded compound materials. For SEM measurements, the plates were broken in liquid nitrogen to prevent thermal deformations. The plate samples were placed in the sample holder, vacuum was applied and SEM images were taken from the broken surface (cross sectional direction).

3 Results and Discussion

3.1 Compounding

The addition of a secondary nanometer sized filling material, especially of carbon blacks, adversely affects the processability of the compound material during extrusion because of high surface and abrasive behaviour. A suitable indicator to describe the melt-viscosity of the compounds is the measured torque during the compounding process and the resulting melt temperature. The higher the torque the higher is the melt viscosity, keeping in mind that a lower melt-viscosity facilitates injection moulding of bipolar plates. The following figures show the obtained torques and temperatures during compounding of the five highly filled materials.

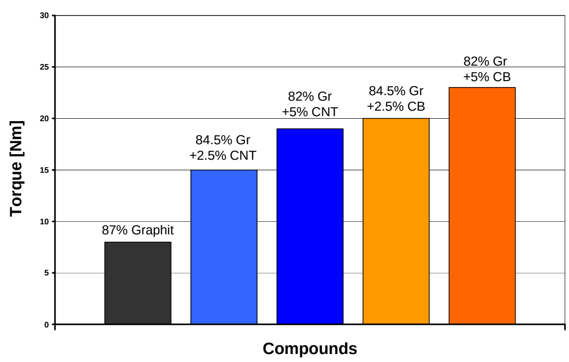

Figure 1: Torque during compounding.

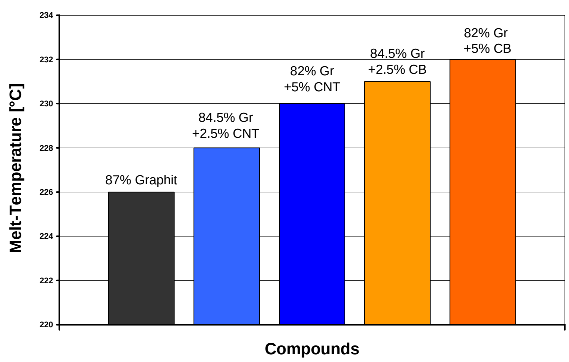

Figure 2: Recorded melt temperature.

As aforementioned the binary graphite/polymer compound shows the lowest torque during compounding. The addition of carbon blacks (CB) or CNTs in hybrid compounds significantly increases the torque and thus the melt temperature. But it can be seen that CNT-based compounds reveal a lower torque-value when compared to their carbon black based counterparts. CNTs tend to be less abrasive than carbon blacks and this induces a lower melt viscosity.

3.2 Electrical conductivity

The following graph shows the area specific volume resistivity of the five investigated compounds, measured at injection moulded material samples.

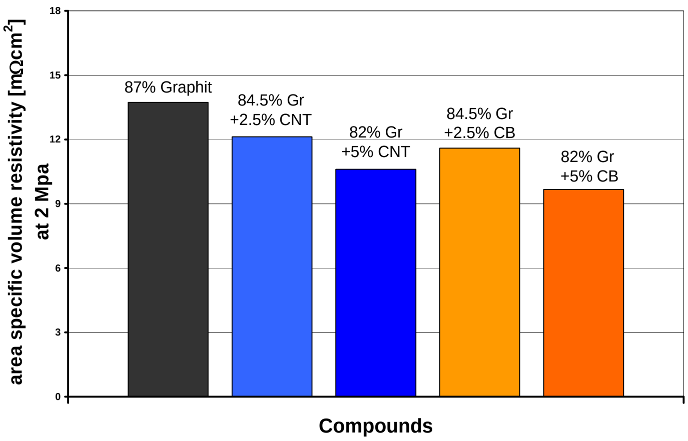

Figure 3: Electrical resistivity.

Figure 4: Injection moulded samples.

The experimental results show that the combination of graphite with carbon blacks or CNTs exhibits a positive effect and leads to lower volume resistivities. It can be seen that there is no significant difference in electrical conductivity between carbon black and CNT filled compound based plates at equal filling content. The addition of the nanometer sized carbon blacks or CNTs forms further conductive bridges through the insulating polymer matrix between the micro sized graphite flakes. Figure 5 and Figure 6 show schematically the differences between binary and hybrid compounds.

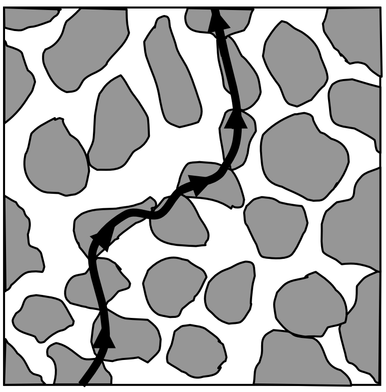

Figure 5: Scheme of a binary system (graphite flakes in a polymer).

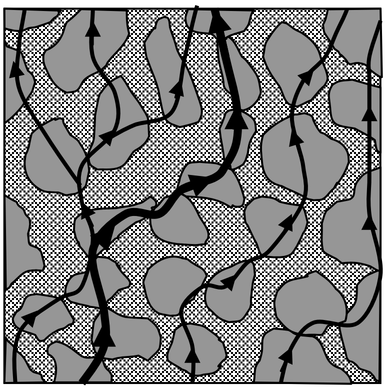

Figure 6: Scheme of a hybrid system (graphite + CB or CNTs in a polymer).

This assumption can be approved by images from scanning electron microscope which give an idea about the internal structure and dispersion of nano particles between graphite flakes at the injection moulded compound materials.

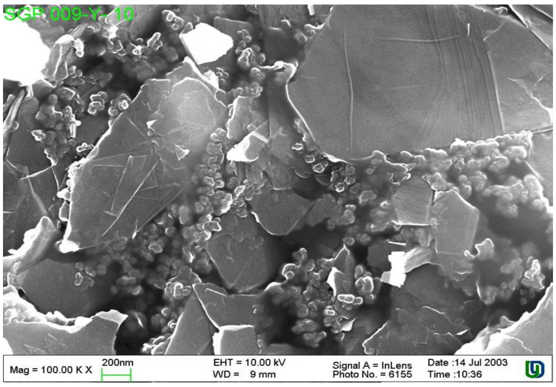

Figure 7: Carbon black between graphite.

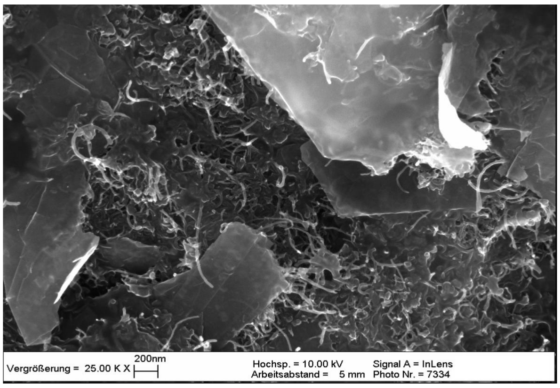

Figure 8: CNTs between graphite flakes.

3.3 Injection moulding and single fuel cell test

Based on the mentioned positive effects of compound material with CNTs, first CNT-based bipolar plates have been injection moulded with a cycle time of 18 seconds for one bipolar plate (Figure 9). Differences in bipolar plate quality in comparison with carbon black based bipolar plates could not be observed so far. A fully automated removal from the bipolar plates out of the injection moulding tool is ensured by robots, to prevent the operator from eventually occurring expositions with CNTs.

A first single fuel cell stack with injection moulded CNT-based bipolar plates has been assembled and the performance has been tested. This first test has been carried out to analyse the appropriateness of CNT-based bipolar plates in principle. It could be observed that CNT-based bipolar plates do function as well as carbon black based bipolar plates in a PEM fuel cell. No significant difference in the cell performance could be observed.

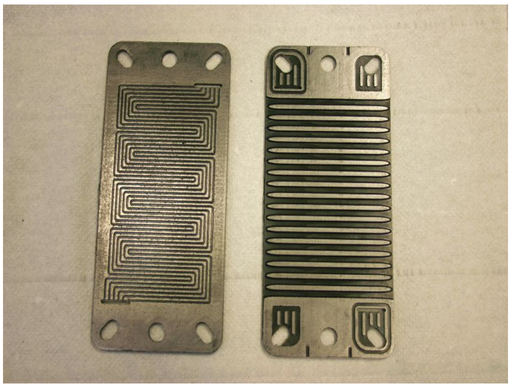

Figure 9: Injection moulded CNT based bipolar plates.

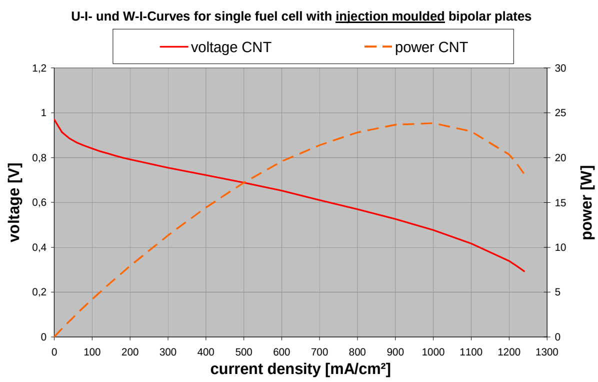

Figure 10: Polarisation-curves for a single fuel cell stack with CNT-based bipolar plates.

4 Conclusion

The combination of nano sized (CNTs) and micro sized (graphite) filling particles in hybrid compounds is chosen as the next step towards optimized bipolar plates for PEM fuel cells. It turned out that CNTs tend to be less abrasive than carbon blacks and this leads to a lower melt viscosity which is required and helpful for the injection moulding process to bipolar plates. Furthermore CNTs do function as bridging particles between the other filling component graphite and this leads to a significantly improved conductivity. Due to their favourable electrical and mechanical properties carbon nanotubes are most probably a promising filling material. There is still a need for more investigations to utilize the unique properties of CNTs in hybrid compounds. Nevertheless, first CNT-based bipolar plates were successfully produced and tested in single fuel cell stacks.

Acknowledgment

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